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(54) Title: DERIVATIVES OF POLYALKYLENEPOLYAMINES AS CORROSION INHIBITORS

(57) Abstract

A composition of polyalkylenepolyamine derivatives useful as a corrosion inhibitor in aqueous media produced by reacting a starting polyalkylenepolyamine composition comprising a mixture of: (i) at least one C-alkyl-ethylene diamine; and (ii) at least one di-(C-alkyl)-diethylenetriamine; wherein each C-alkyl group on the ethylene diamine and diethylenetriamine independently contain between 8-26 carbon atoms; with a derivatizing agent which is either an alkylating agent or an alkylene oxide. Methods for preparing this composition and using it to inhibit the corrosion of corrodible metal alloys are also disclosed.

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1 DERIVATIVES OF POLYALKYLENEPOLYAMINES
2 AS CORROSION INHIBITORS

3
4 BACKGROUND OF THE INVENTION

5
6 This invention relates to compositions comprising
7 polyalkylenepolyamine derivatives which demonstrate
8 improved properties as corrosion inhibitors when used in
9 substantially aqueous media. This invention further
10 concerns a method of making compositions of these
11 water-soluble, polyalkylenepolyamine derivatives by
12 reacting a hydrocarbon-soluble polyalkylenepolyamine
13 composition with either an alkylating agent or an alkylene
14 oxide. Additionally, this invention also relates to
15 methods for using the polyalkylenepolyamine derivatives as
16 effective corrosion inhibitors capable of protecting metal
17 surfaces placed in contact with potentially corrosive
18 chemicals.

19
20 Increasingly, industrial companies have begun to realize
21 the economic importance of maintaining their equipment to
22 ensure the longest operating life possible. This has been
23 particularly true in the area of oil field operations.

24
25 As oil companies have been forced to go to new lengths in
26 their search for oil, their operating equipment has also
27 become more expensive and difficult to easily replace.

28
29 Given this level of investment, most companies have
30 increasingly sought to rely on corrosion inhibitors to
31 protect the metal surfaces on their drilling rigs and
32 pipelines from the corrosive effects of the chemicals
33 found in underground environments.

34
35 These corrosion inhibitors can either be applied directly
36 to the potentially affected metal parts or injected into
37 the oil well containing the corrosive chemicals. To

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1 achieve maximum effectiveness, the corrosion inhibitors
2 should be dispersible or miscible in this underground
3 medium.

4
5 Historically, alkylamines or polyamines have been the most
6 commonly used corrosion inhibitors in oil well operations.
7 A recent invention has also created compositions of
8 polyalkylenepolyamines which are purported to possess even
9 better corrosion inhibition properties. These chemical
10 compositions are hydrocarbon-soluble, however, and
11 experience in the field has shown that they are of limited
12 effectiveness in the substantially aqueous environments
13 one can potentially confront when drilling for oil. Since
14 the base amines of these compositions are insoluble in an
15 aqueous medium, they simply cannot work to maximum
16 effectiveness as corrosion inhibitors in water-based
17 environments.

18
19 The instant invention offers the ability to solve this
20 limitation presently hampering these types of corrosion
21 inhibitors. It proposes methods for the derivatization of
22 polyalkylenepolyamine compositions into novel compositions
23 of derivatized polyalkylenepolyamines.

24
25 These novel chemical compositions demonstrate increased
26 water solubility, making them more effective in the
27 heavily aqueous corrosive media, which are increasingly
28 encountered in the ever-expanding search for new sources
29 of oil.

30
31 In traditional oil production operations, the drilling
32 rods are introduced into a subsurface environment largely
33 consisting of hydrocarbon compounds. While some water is
34 theoretically present in all wells, the corrosion and
35 pitting which occur in these situations are largely the
36 result of the effects of the hydrocarbon compounds on the
37 rod. As noted previously, to achieve maximum

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1 effectiveness, a corrosion inhibitor should be dispersible
2 in the medium in which it is to operate. Thus, the
3 standard hydrocarbon-soluble amine or
4 polyalkylenepolyamine composition provides adequate
5 coverage in most "typical" oil production operations.

6
7 Increasingly, however, as our domestic supply of oil
8 continues to dwindle, many oil companies are being forced
9 to expand their quest for this valuable resource into many
10 non-traditional areas. For example, a large percentage of
11 the new wells being drilled are in substantially aqueous
12 environments, presenting an even greater need to monitor
13 the effects of corrosion on operating efficiency.

14
15 Numerous experiments have repeatedly demonstrated that the
16 presence of water in underground environments greatly
17 speeds up pitting and corrosion processes. Many new wells
18 are affected by CO₂ corrosion resulting from the carbonic
19 acid which forms when CO₂ comes in contact with water.
20 Additionally, oxygen entering a heavily aqueous well also
21 reacts with water in a manner that speeds up the effects
22 of corrosion. Thus, it is especially vital to use
23 effective corrosion inhibitors when operating in
24 substantially aqueous media in order to counteract the
25 added threat of corrosion in this type of environment.

26
27 Unfortunately, base amines and their more specialized
28 polyalkylenepolyamine counterparts have not proven
29 effective in these situations. Because most of these
30 compounds are highly insoluble in water, when they are
31 applied to drilling rods being used in substantially
32 aqueous environments, they have shown a tendency to
33 migrate from water, which is usually the layer in direct
34 contact with the drilling rods, and dissolve in the
35 hydrocarbon layer. With no protection between the
36 dangerous aqueous layer and the drilling rod, corrosion
37 proceeds relatively unabated.

1 Many in industry have attempted to solve this problem by
2 searching for corrosion inhibitors which are dispersible
3 in water, and thus effective in heavily aqueous media.
4 The instant invention represents a successful culmination
5 of one individual's efforts in this regard.

6

7 Numerous patents describe polyalkylenepolyamine compounds,
8 their derivatives, and the processes for their production.

9

10 U.S. Patent No. 4,314,083 discloses a process for
11 selectively preparing non-cyclic polyalkylenepolyamine
12 compounds by reacting an alkylenepolyamine compound with a
13 hydroxy compound in the presence of a catalytically
14 effective amount of salt, nitrogen, or sulfur-containing
15 substance. This process is limited to short-chain alkyl
16 groups consisting of no more than 4 carbon atoms.

17

18 U.S. Patent No. 3,565,941 discloses a process for
19 alkylating a polyalkylenepolyamine by first reacting the
20 polyamine with an acid and then following with either an
21 alkylating agent or a polyamine salt. This process is
22 also specifically limited to hydrogen or short-chain alkyl
23 groups of methyl or ethyl. The products also have limited
24 uses as chemical intermediates, monomers, bases and
25 flocculating agents.

26

27 Various other amine compounds have been recognized by the
28 scientific community as effective in minimizing the
29 corrosion of metal alloys. Prior patents disclose
30 numerous quaternary, rosin and fatty amine compounds, as
31 well as their corresponding derivatives, all of which are
32 considered to be most beneficial in specific types of
33 industrial operations. Alkylamines and polyamines are
34 also accepted as particularly effective corrosion
35 inhibitors in oil field operations. For years, however,
36 researchers have been attempting to further refine these
37 compounds in the hopes of developing other compositions

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1 which demonstrate even better corrosion inhibition
2 properties.
3
4 U.S. Patent No. 4,900,458, which is incorporated by
5 reference in its entirety herein, represents a major
6 success in this regard. Here, Schroeder et al. discovered
7 methods for manufacturing novel polyalkylenepolyamine
8 compositions in which an alkyl group of between 10-28
9 hydrocarbons was attached to the carbon atom instead of
10 the nitrogen. This structural modification was shown to
11 enable these hydrocarbon-soluble compositions to exhibit
12 improved corrosion inhibition properties in oily media.
13
14 In contrast, the present invention provides excellent
15 corrosion inhibitors useful in substantially aqueous
16 media.
17

18 SUMMARY OF THE INVENTION

19
20 The instant invention relies upon the
21 polyalkylenepolyamine compositions of U.S. Patent No.
22 4,900,458 as its starting material. These compositions
23 are reacted with either an alkylene oxide or an alkylating
24 agent to yield highly water-soluble or dispersible
25 derivatives of polyalkylenepolyamines. These derivatives
26 demonstrate surprisingly improved abilities as corrosion
27 inhibitors when used in aqueous media, far surpassing the
28 results obtained by known basic amine inhibitors or the
29 more specialized polyalkylenepolyamine starting materials
30 referred to above.
31

32 This invention provides compositions of
33 polyalkylenepolyamine derivatives which offer improved
34 corrosion inhibition properties when used in substantially
35 aqueous media. Specifically, but without limitation,
36 these compositions are uniquely effective in certain
37 operations involving the production and transportation of

-6-

1 oil. In a preferred embodiment, the amine groups of the
2 polyalkylenepolyamines are methylated prior to
3 derivatization, with for example an alkyl halide or a
4 dialkyl sulfate.

5
6 The instant invention provides a substantially
7 water-soluble, corrosion-inhibiting, composition of
8 polyalkylenepolyamine derivatives. This composition is
9 obtained by reacting a mixture containing: (i) at least
10 one C-alkyl-ethylene diamine and (ii) at least one
11 di-(C-alkyl)-diethylenetriamine; wherein each C-alkyl
12 group on the ethylene diamine and diethylenetriamine
13 independently contains from 8-26 carbon atoms, with
14 specially selected alkylating agents or an alkylene oxide,
15 preferably ethylene oxide. In a preferred embodiment, the
16 amine groups of the polyalkylenepolyamines are methylated
17 prior to derivatization, with for example, an alkyl halide
18 or a dialkyl sulfate.

19
20 The instant invention also relates to a method of
21 inhibiting corrosion on corrodible metals by directly
22 applying the derivatized polyalkylenepolyamine composition
23 to the potentially affected metal.

24
25 The instant invention also has specific applications in
26 the oil production industry. It encompasses a method for
27 inhibiting corrosion on corrodible metals used in or
28 around substantially aqueous oil wells which involves
29 injecting the composition of polyalkylenepolyamine
30 derivatives directly into the underground oil well
31 environment.

32
33 Among other factors, the instant invention is based on our
34 discovery that a mixture of derivatized C-alkyl-ethylene
35 diamines and di-(C-alkyl)-diethylenetriamines, wherein
36 each alkyl group independently contains from 8-26 carbon
37 atoms, demonstrate excellent corrosion inhibition

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1 potential in substantially aqueous media. Because these
2 derivatized polyalkylenepolyamine mixtures are water
3 dispersible, they give at least 85% inhibition of CO₂
4 corrosion, and preferably greater than 90% inhibition, in
5 the industry-standard wheel test with NACE brine.
6 Preferred compositions are effective in the 250 to 25 ppm
7 concentration range.

8

9

DETAILED DESCRIPTION OF THE PREFERRED

10

EMBODIMENTS OF THE INVENTION

11

12 The instant invention provides a water-soluble composition
13 of polyalkylenepolyamine derivatives which exhibit
14 excellent corrosion inhibition properties when used in
15 substantially aqueous media. The instant invention
16 further discloses methods of producing derivatized
17 compounds by reacting specific polyalkylenepolyamine
18 compounds with specially selected alkylating agents or
19 alkylene oxides. Useful alkylating agents are those that
20 react with primary, secondary or tertiary amines to make
21 ammonium salts.

22

23 The terms "heavily aqueous" and "substantially aqueous"
24 are used extensively and interchangeably throughout this
25 application. As referred to herein, these terms are used
26 to describe an environment that consists of more water
27 than hydrocarbons. Preferably this ratio will be greater
28 than 3 parts water to 1 part oil.

29

30 The specific derivatized compounds which are intended to
31 be covered by this application are referred to as being
32 either "soluble" or "dispersible" in water. Preferably,
33 these compounds will possess a water dispersibility rating
34 under 10 rating units, as measured by a Water
35 Dispersibility Test using NACE brine as discussed in
36 detail in Example 12. Ratings lower than 10 also reflect

1 formulations which have a partition coefficient between
2 water and octyl alcohol ≤ 2 .

3

4 As used herein, the terms "reaction" or "reacting" shall
5 be taken to mean a chemical change that occurs by
6 combination, replacement, decomposition or some
7 modification thereof.

8

9 As used herein, the term "derivatized" shall be taken to
10 mean the reaction of at least one of the
11 polyalkylenepolyamine nitrogens with an alkylating or
12 alkoxyating agent, i.e., with a derivatizing agent. When
13 more than one of the nitrogens of a polyalkylenepolyamine
14 structure are reacted with an alkylating or alkoxyating
15 agent, the product is termed herein as "polyderivatized."

16

17 The Starting Polyalkylenepolyamines

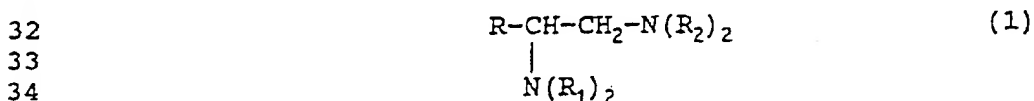
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19 Polyalkylenepolyamine compounds that can be used to
20 produce my derivatized compositions are disclosed in
21 detail in U.S. Patent No. 4,900,458. The instant
22 invention directly incorporates by reference the specific
23 chemical compositions and their methods of preparation as
24 described in detail therein.

25

26 The polyalkylenepolyamine compositions which provide the
27 foundation for the instant invention contain a mixture of
28 compounds. This mixture includes at least one
29 C-alkyl-ethylene diamine as described in Structure 1
30 below.

31



35

36 In Structure 1, R is an alkyl group containing 8 to 26
37 carbon atoms. R₁ and R₂ individually can be any

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1 combination of hydrogen or lower alkyl groups. The terms
 2 "lower alkyl" and "lower alkyl group" mean alkyl groups
 3 from 1 to 5 carbon atoms, more preferably methyl or ethyl.
 4 Preferred compositions include those where the R group
 5 contains between 10 and 22 carbon atoms, preferably
 6 between 10 and 16, more preferably 12 and/or 14 carbon
 7 atoms; and where at least one of the R₁ or R₂ groups are
 8 lower alkyl, preferably where a plurality of these R
 9 groups are lower alkyl.

10

11 The starting polyalkylenepolyamines can be made from alpha
 12 olefins via epoxidation and reaction with amines, for
 13 example ammonia, in the presence of an amination catalyst.
 14 For example, see U.S. Patent No. 4,900,458. To clarify
 15 the nomenclature used herein: a C₁₄ alpha olefin produces
 16 a C₁₄ epoxide which in turn produces a C₁₄
 17 polyalkylenepolyamine. The C₁₄ epoxide has an alkyl group
 18 of 12 carbon atoms on the epoxide ring and this produces
 19 polyalkylenepolyamines with alkyl groups of 12 carbon
 20 atoms.

21

22 The starting polyalkylenepolyamine composition also
 23 contains at least one di-(C-alkyl)-diethylenetriamine as
 24 detailed in Structure 2 below.

25

26

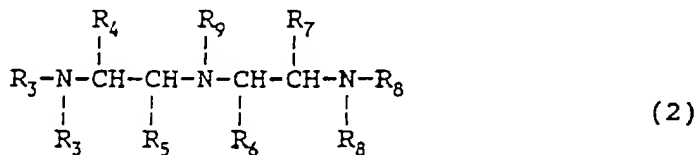
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28

29

30

31



32 In Structure 2, R₄, R₅, R₆ and R₇ individually may be
 33 hydrogen or alkyl of 8 to 26 carbon atoms, provided that
 34 two of the R₄, R₅, R₆ and R₇ groups are hydrogen and two are
 35 alkyl. In Structure 2, R₃, R₈ and R₉ can individually be
 36 any combination of hydrogen and lower alkyl groups, as
 37 described above. Methods of preparing compounds of
 38 Structure 1 when R₁ and R₂ comprise methyl or compounds of

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1 Structure 2 when R_3 , R_8 and R_9 comprise methyl are
2 disclosed in Examples 1C, 1D, and 1E, below.

3
4 In a preferred embodiment, reaction of an amine hydrogen
5 (i.e., N-H) with formic acid and formaldehyde results in
6 an N-methylated amine, where the N-H group has been
7 converted to an N-CH₃ group. When there is more than one
8 N-H group in a molecule (such as in the polyalkylene
9 polyamines of U.S. Patent No. 4,900,458) reaction with
10 formic acid and formaldehyde will partially or totally
11 convert all the N-H groups to N-CH₃ groups, depending on
12 the reaction conditions and amounts of reactants.
13 Substantially complete conversion is preferred. Another
14 method of preparing compounds where R_1 , R_2 , R_3 , R_8 and/or R_9
15 are lower alkyl is to use alkyl amines, such as methyl
16 amine or dimethyl amine, instead of ammonia in the
17 preparation procedures disclosed in U.S. Pat. No.
18 4,900,458 for the starting polyalkylenepolyamines.

19
20 As used herein, the term "N-methylated"
21 polyalkylenepolyamines refers to the above-described
22 polyalkylenepolyamines having one or two methyl groups on
23 some or all of the amine nitrogens. When there are two
24 methyl (or lower alkyl) groups on the nitrogen, alkylation
25 -- for example with an alkyl halide -- results in a
26 quaternary amine salt (a "quat") having a total of four
27 alkyl groups on the nitrogen. These N-methylated
28 polyalkylenepolyamines are useful as corrosion inhibitors
29 in their own right, and are especially preferred
30 compositions for preparing the polyalkylenepolyamine
31 derivatives of this invention. These N-methylated
32 polyalkylenepolyamines are preferred in part because of
33 their lower meltpoints, as measured by differential
34 scanning calorimetry. Lower meltpoints are economically
35 advantageous in that less heat is required to melt the
36 polyalkylenepolyamines prior to derivatization or
37 formulation. Also, these N-methylated

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1 polyalkylenepolyamines are easier to apply in corrosion
2 applications.

3

4 The terms "C-alkyl" and "di-(C-alkyl)" are also used at
5 numerous points throughout this application. "C-alkyl" is
6 meant to encompass any alkyl group that is directly bonded
7 to a carbon atom in Structure 1, i.e. the R group.
8 "Di-(C-alkyl)" refers to two alkyl groups which are each
9 directly bonded to two different carbon atoms in Structure
10 2, i.e., two of the groups at R₄, R₅, R₆, or R₇.

11

12 Preparation of Polyalkylenepolyamine Derivatives

13

14 The water-soluble or water-dispersible
15 polyalkylenepolyamine derivatives which are the subject of
16 the instant invention are prepared by reacting the
17 polyalkylenepolyamine mixtures of Structures 1 and 2 with
18 various alkylating agents or alkylene oxides. Two
19 preferred methods of preparation are outlined below.

20

21 1. Alkylation of the Polyalkylenepolyamines

22

23 A preferred method for obtaining derivatives of
24 polyalkylenepolyamines is to react a polyalkylenepolyamine
25 mixture containing Structure 1 and Structure 2 with an
26 alkylating agent, BX. In this process, alkylation can
27 occur on any single nitrogen, all the nitrogen centers, or
28 any combination thereof. The derivatized versions of
29 Structures 1 and 2 resulting from this reaction are shown
30 in Structures 3 and 4, respectively.

31

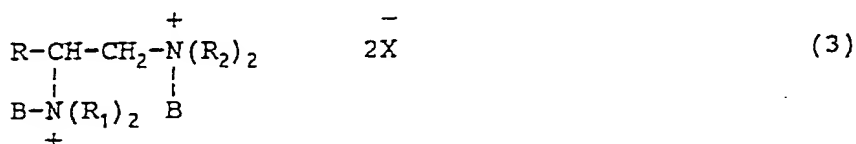
32 The starting polyalkylenepolyamines can also be N-
33 methylated by reaction with formic acid and formaldehyde
34 as described in Examples 1C, 1D, 1E and 1F. These N-
35 methylated products can then be alkylated to produce
36 quaternary amine salts of this invention.

37

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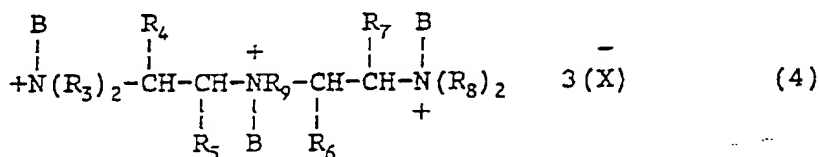
1 The derivatized water-soluble polyalkylenepolyamine
 2 composition consists of a mixture containing: (a) at
 3 least one derivatized C-alkyl-ethylene diamine as
 4 described in Structure 3 and (b) at least one derivatized
 5 di-(C-alkyl)-diethylenetriamine as described in Structure
 6 4. Each C-alkyl group in the derivatized ethylene diamine
 7 and diethylenetriamine independently contains from 8-26
 8 carbon atoms.

9
 10 The derivatized C-alkyl-ethylene diamine is an ammonium
 11 salt described by Structure 3 below.



12
 13
 14
 15
 16
 17
 18
 19 In Structure 3, R is an alkyl group containing 8 to 26
 20 carbon atoms. R_1 and R_2 individually can be hydrogen,
 21 lower alkyl, or any combination thereof. B is derived
 22 from the alkylating agent. Polyammonium salts having all
 23 the amine nitrogens alkylated are preferred.

24
 25 A preferred derivatized di-(C-alkyl)-diethylenetriamine
 26 ammonium salt is described by Structure 4 below.



27
 28
 29
 30
 31
 32
 33
 34
 35 In Structure 4, R_4 , R_5 , R_6 and R_7 individually can be
 36 hydrogen or alkyl of 8 to 26 carbon atoms, provided that
 37 two of the R_4 , R_5 , R_6 and R_7 groups are hydrogen and two are
 38 alkyl. R_3 , R_8 and R_9 can individually be any combination
 39 of hydrogen and lower alkyl groups. B is derived from the
 40 alkylating agent as described below. Polyammonium salts
 41 having all the amine nitrogens alkylated are preferred.

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1 In both derivatized structures, the alkylating agent's
2 alkyl group, B, can be an alkyl or aryl group, benzyl or
3 alkylcarboxylate. Preferred alkyl groups are methyl,
4 ethyl and benzyl. The anion, X, can be a halogen,
5 including chloride, bromide and iodide, a sulfate, such as
6 $O-SO_3-R$ or an equivalent anion which is readily displaced
7 by the nucleophilic nitrogen of the amine. These types of
8 anions are well known to those skilled in the art.
9 Preferred leaving groups are chloride and methylsulfate.
10 Preferred alkylating agents include benzyl chloride,
11 methyl chloride, alpha-chloroacetic acid, dimethyl
12 sulfate, and alpha-chloromethyl phosphoric acid.

13

14 It is preferable to react all of the amine nitrogens with
15 the derivatizing agent, although partial derivatization
16 can occur. The ratio of alkylating agent to
17 polyalkylenepolyamine nitrogen can be from 20:1 to 0.05:1
18 on a molar basis; more preferably the ratio is from 2:1 to
19 1:1.

20

21 In one embodiment the present invention is a composition
22 containing derivatives of polyalkylenepolyamines
23 comprising mixtures of (i) at least one C-alkyl-ethylene
24 diamine polyammonium salt and (ii) at least one di-(C-
25 alkyl)-diethylenetriamine polyammonium salt. Here each C-
26 alkyl group on the ethylene diamine and the
27 diethylenetriamine independently contains between 8-26
28 carbon atoms. These polyammonium salts have more than one
29 of the nitrogens of each of the derivatized
30 polyalkylenepolyamines having a positive charge;
31 preferably substantially all the nitrogen atoms of both
32 components (i) and (ii) are positively charged. It is
33 preferred to have polyammonium salts -- salts with more
34 than a single positive charge. These
35 polyalkylenepolyamine derivatives are also be described as
36 polyderivatized.

37

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1 Preferred derivatized products include alkylation products
2 of alkyl halides and sulfates with N-methylated
3 polyalkylene polyamines.

4

5 More preferred derivatized products include (1) the
6 products obtained by the reaction of benzyl chloride with
7 N-methylated C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, and C₂₀₋₂₄ polyalkylene
8 polyamines and mixtures thereof; (2) the products obtained
9 by the reaction of methyl chloride with N-methylated C₁₀,
10 C₁₂, C₁₄, C₁₆, C₁₈, and C₂₀₋₂₄ polyalkylenepolyamines and
11 mixtures thereof; (3) the products of the reaction of
12 dimethyl sulfate with N-methylated C₁₀, C₁₂, C₁₄, C₁₆, C₁₈,
13 and C₂₀₋₂₄ polyalkylenepolyamines and mixtures thereof; (4)
14 the products of the reaction of alpha-chloromethyl
15 phosphoric acid with C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, and C₂₀₋₂₄
16 polyalkylenepolyamines and mixtures thereof; and (5) the
17 products obtained by the reaction of alpha-chloromethyl
18 phosphoric acid with N-methylated C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, and
19 C₂₀₋₂₄ polyalkylenepolyamines and mixtures thereof.
20 Especially preferred products are prepared from C₁₂, C₁₄, or
21 C₁₆ polyalkylenepolyamines, more preferably from C₁₄ and C₁₆
22 polyalkylenepolyamines.

23

24 Mixtures of polyalkylenepolyamines having more than one
25 carbon number can be used as the starting material; for
26 example, mixtures of C₁₀ polyalkylenepolyamines with C₁₄
27 polyalkylenepolyamines are useful corrosion inhibitors
28 when derivatized. Preferred derivatives are extremely
29 dispersible or soluble in water, making them effective
30 corrosion inhibitors in substantially aqueous media.

31

32 2. Alkoxylation of the Polyalkylenepolyamines

33

34 A second method for obtaining a polyalkylenepolyamine
35 derivative of this invention is to react a
36 polyalkylenepolyamine mixture containing Structures 1 and
37 2 with an alkylene oxide. Alkoxylation of amines is well

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1 known in the art. Typical reaction conditions include
 2 temperature in the range of 80-100°C and elevated
 3 pressure. This reaction produces a mixture of at least
 4 one N-alkoxylated C-alkyl-ethylenediamine and at least one
 5 N-alkoxylated di-(C-alkyl)-diethylenetriamine.

6

7 An N-alkoxylated C-alkyl-ethylenediamine of this invention
 8 is exemplified by Structure 5 below.

9

10

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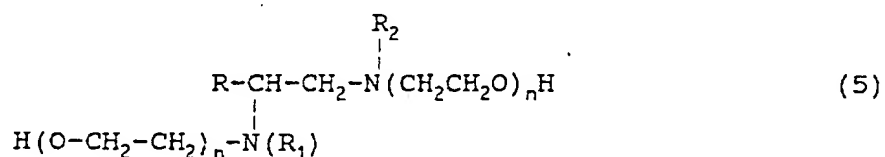
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15

16



17 In Structure 5, R is an alkyl group containing 8 to 26
 18 carbon atoms. R₁ and R₂ individually can be any
 19 combination of hydrogen and lower alkyl groups. Each n is
 20 independently between 0 and 4, with the sum of all n's
 21 being at least 1.

22

23 An N-alkoxylated di-(C-alkyl)-diethylenetriamine is
 24 described by a modified version of Structure 2, in which
 25 some or all of the R₃, R₈ and R₉ groups are ethoxy or
 26 polyethoxy, (CH₂CH₂O)_nH, and each n is independently
 27 between 0 and 4, with the sum of all n's being at least 1.

28

29 In one embodiment the present invention is a composition
 30 containing derivatives of polyalkylenepolyamines
 31 comprising a mixture of (i) at least one C-alkyl-ethylene
 32 diamine poly-N-ethoxylate and (ii) at least one di-(C-
 33 alkyl)-diethylenetriamine poly-N-ethoxylate. Here each C-
 34 alkyl group on the ethylene diamine and the
 35 diethylenetriamine independently contains between 8-26
 36 carbon atoms. In these poly-N-ethoxylated compositions,
 37 at least one of the nitrogens of each of the derivatized
 38 polyalkylenepolyamines has an ethoxy group (n=1) or a
 39 polyethoxy group (n>1), e.g., in the (-CH₂-CH₂-O-)_n-H

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1 group of structures. Preferably substantially all the
2 nitrogen atoms of both components (i) and (ii) are
3 ethoxylated or polyethoxylated. These
4 polyalkylenepolyamine derivatives can also be described as
5 poly-derivatized.

6
7 Preferred ethoxylation agents are alkylene oxides such as
8 ethylene oxide and propylene oxide; ethylene oxide is most
9 preferred. The ratio of alkoxyating agent to amine
10 nitrogen in the polyalkylenepolyamine can be in the range
11 of from 100:1 to 0.5:1. Preferably it is in the range of
12 from 10:1 to 1:1, more preferably 8:1 to 2:1. The amount
13 of amine nitrogen is based on the total amine content of
14 the polyalkylenepolyamine.

15
16 The derivatized, water-soluble polyalkylenepolyamine
17 composition consists of a mixture containing: (a) at
18 least one N-alkoxylated C-alkyl-ethylene diamine as
19 described in Structure 5 and (b) at least one N-
20 alkoxylated di-(C-alkyl)-diethylenetriamine as described
21 hereinabove. Each C-alkyl group in the derivatized
22 ethylene diamine and diethylenetriamine independently
23 contains from 8-26 carbon atoms.

24 25 Corrosion Inhibition

26
27 Some of the derivatized polyalkylenepolyamine compositions
28 of this invention have turned out to be surprisingly good
29 corrosion inhibitors in heavily aqueous media. Because
30 they are dispersible in the aqueous layer which is usually
31 in direct contact with the corrodible metals or metal
32 alloys, they demonstrate superior performance over other
33 commercially-available, hydrocarbon-soluble, corrosion
34 inhibitors. These compositions are particularly effective
35 at inhibiting the corrosion which can occur on oil
36 drilling rods and in underground pipelines used to
37 transport oil.

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1 The ability of these derivatized polyalkylenepolyamine
2 compositions to act as effective corrosion inhibitors in
3 these situations rests in part on the length of the alkyl
4 group associated with each of the individual derivatized
5 compounds. As has been noted in detail throughout this
6 application, the alkyl groups which are part of our
7 derivatized polyalkylenepolyamines are relatively long
8 chains containing from 8 to 26 carbon atoms. Preferably,
9 these chains will be between 8 and 16 carbons in length,
10 more preferably between 10 and 14 carbon atoms.

11

12 Not wishing to be bound by any theory, it is believed that
13 the length of the alkyl group affects the corrosion
14 inhibition properties of the derivatized
15 polyalkylenepolyamines. The nitrogen atoms which are part
16 of these derivatized compounds are relatively polar and
17 have been found to adhere to the potentially affected
18 metal alloy. The long chain alkyl groups essentially form
19 a "tail" which is very lipophilic in nature. When enough
20 derivatized polyalkylenepolyamines are present, the
21 hydrophobicity of these alkyl "tails" acts as a barrier
22 and prevents corrosive oxygen and sulfur molecules from
23 attacking the metal. Short alkyl chains on these
24 polyalkylenepolyamines do not provide the coverage
25 necessary to give effective corrosion inhibition.

26

27 In standard wheel tests using NACE brine at 90°C tested in
28 saturated CO₂ solution, various formulations of the
29 derivatized polyalkylenepolyamine compositions of this
30 invention provided at least 85% corrosion inhibition at
31 125 ppm of inhibitor. Most often, these compositions
32 provided greater than 90% corrosion inhibition. These
33 same compounds also demonstrated dispersibility ratings
34 under 10 rating units as determined by the Water
35 Dispersibility Test using NACE Brine as outlined in
36 Example 12. It is the combination of these two factors

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1 which ensures effective corrosion inhibition in heavily
2 aqueous environments.

3
4 The instant invention also relates to methods for using
5 the derivatized polyalkylenepolyamine compositions as
6 effective corrosion inhibitors. It is preferred to
7 deliver the derivatized compositions to the potentially
8 affected metal surface in a continuous process at a
9 concentration ranging from 1 ppm - 1000 ppm, preferably
10 from 5 ppm - 200 ppm, and most preferably between 10 ppm -
11 100 ppm. Batch delivery in larger doses is also
12 acceptable.

13
14 For use as corrosion inhibitors, the derivatized
15 polyalkylenepolyamines of the invention are applied to the
16 metal surfaces to be protected in a variety of ways known
17 in the art. For example, a dilute aqueous solution of the
18 derivatized polyalkylenepolyamine may be contacted with
19 the metal to be protected, using methods such as dipping,
20 spraying, wiping, and the like. For this method of
21 application, solutions of about 0.1 to 10%, preferably
22 from about 0.2 to 1%, by weight of derivatized
23 polyalkylenepolyamine, or mixtures of derivatized
24 polyalkylenepolyamine and other active corrosion
25 inhibiting agents, are employed.

26
27 Alternatively, water-dispersible formulations of the
28 present derivatized polyalkylenepolyamines, or mixtures of
29 the derivatized polyalkylenepolyamines and other active
30 corrosion inhibiting agents, can be added to a corrosive
31 aqueous environment. In this method of application,
32 sufficient amounts of derivatized polyalkylenepolyamines,
33 or mixtures of the derivatized polyalkylenepolyamines and
34 other active corrosion inhibiting agents, are added to
35 give from about 1 to 1,000 ppm, preferably from 10 to 200
36 ppm, of active corrosion inhibitor in the final solution
37 for continuous methods of treatment. For batch treatment

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1 methods, the level of corrosion inhibiting agents is
2 generally between 500 and 25,000 ppm, preferably between
3 500 and 5,000 ppm.

4

5 Generally, corrosion inhibitors are formulated with other
6 components for corrosion inhibiting application.
7 Preferably, the corrosion inhibiting derivatized
8 polyalkylenepolyamine composition of the present invention
9 will be combined with one or more dimer/trimer acids to
10 provide a formulated product. Dimer/trimer acids are
11 well-known in the art and are typically derived from fatty
12 acids. Examples of dimer/trimer acids include Empol 1024,
13 Empol 1041 and Empol 1052, obtained from Emery Chemicals.

14

15 In addition to the derivatized polyalkylenepolyamine of
16 the invention and the dimer/trimer acid, corrosion
17 inhibiting formulations may also contain one or more
18 surfactants, one or more alcohols, a small amount of a
19 hydrocarbon and water. The surfactant employed may be
20 ionic or nonionic in nature. The hydrocarbon may be any
21 of the known solvents, such as kerosene, high aromatic
22 distillate, diesel fuel, paint thinner, toluene,
23 lubricating oil, and similar materials. A typical
24 hydrocarbon is kerosene. Isopropanol or methanol are
25 typical alcohols useful as solvents. Formulations
26 containing at least 20 wt % water and/or alcohol are
27 preferred.

28

29 Generally, the active corrosion inhibiting agents will be
30 combined with a solvent and a surface-active agent to
31 produce a concentrated solution of the corrosion
32 inhibitor. In this solution, the derivatized
33 polyalkylenepolyamine, or mixture of the derivatized
34 polyalkylenepolyamine and other active corrosion
35 inhibiting agents, will be present in amounts ranging from
36 about 10 to 60%, preferably about 30 to 50%, by weight.
37 The amount of solvent present is from about 30 to 80%, and

-20-

1 the amount of surfactant is about 1 to 20%, by weight.
2 This concentrated formulation is then diluted to the
3 desired concentration of the final solution.
4
5 A typical water-dispersible formulation will contain about
6 15 to 30% of the present derivatized
7 polyalkylenepolyamine, about 15 to 30% of a dimer/trimer
8 acid, about 1 to 10% of a nonionic surfactant, about 0 to
9 10% of a hydrocarbon solvent, such as kerosene, and about
10 10 to 40% of an alcohol, such as isopropanol or methanol.
11
12 Water-dispersible formulations of the present derivatized
13 polyalkylenepolyamines are particularly useful in brine/CO₂
14 or brine/H₂S environments, such as encountered in oil
15 wells, especially oil wells employing secondary oil
16 recovery techniques.
17
18 The following examples illustrate the basic principles of
19 this invention. They are not to be construed as limiting
20 the invention in any way except as indicated by the
21 appended claims.

22 EXAMPLES

23 Example A

24 MEASUREMENT OF TOTAL AMINE VALUE (TAV)

25
26
27
28 Total Amine Value (TAV), or Total Base Number (TBN) was
29 measured using an ORION 960 autochemistry system sold by
30 Orion Research Inc. The method is described in the Orion
31 960 Instruction Manual (1988) using the Gran function and
32 technique 10. The TAV is the quantity of acid, expressed
33 in term of the equivalent number of mg of KOH, that is
34 required to neutralize all basic constituents present in 1
35 g of sample.

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Example B

NITROGEN CONTENT

The weight percent nitrogen is determined using a Carlo Erba 1500 Nitrogen Analyzer. Nitrogen compounds were converted to nitrogen gas and detected with a thermal conductivity detector. Samples were weighted into a tared tin cup which was crimped and placed in an autosampler. The sample was dropped into a heated tube and totally combusted with oxygen over copper oxide and Cr_2O_3 catalysts. The combustion gases and helium carrier gas were swept through a reduction tube filled with copper metal fines to reduce nitrogen oxides to nitrogen gas. Water, and carbon dioxide were then scrubbed using 3A molecular sieves and ascarite. The remaining gas passed through a gas chromatographic column. The total amount of nitrogen was calculated by assuming that peak area is proportional to amount of nitrogen. Weight percent nitrogen in the sample was found by dividing the total amount of nitrogen by the sample weight.

Example 1 - Procedures For Preparing Starting Materials

Outlined below are the typical procedures used to prepare polyalkylenepolyamine and methylated polyalkylenepolyamine compositions which serve as the starting materials for the compositions of this invention. Examples 1A to 1F describe useful methods of preparing these starting materials.

Examples 2-11 exemplify methods for making specific polyalkylenepolyamine derivatives. These procedures can readily be modified by those skilled in the art for polyalkylenepolyamines having different carbon numbers.

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Example 1APREPARATION OF C₁₀ POLYALKYLENEPOLYAMINE

To a 1-liter autoclave equipped with an air-drive stirrer 250 g of C₁₀ epoxide (prepared from a decene heartcut), 38 g of wet Raney Nickel catalyst, and 16 cc of distilled water were added to 450 cc of liquid ammonia and 40 psig of hydrogen.

The mixture was stirred at 1500 rpm for 45 minutes until the composition reached 185°C. This temperature was maintained with stirring for 2.5 hours. The maximum pressure during the reaction was 2800 psig. The composition was then cooled to a temperature of 100°C while stirring at 150 rpm. Excess ammonia was vented and the product was filtered to remove catalyst. A semisolid waxy amine product (243 g) was obtained. Structure of the product was confirmed by NMR. The product had a TAV of 367, and a DSC endpoint of 152°F.

Polyalkylenepolyamines of other carbon chain lengths were prepared from the corresponding epoxides using this procedure and adjusting the amounts charged to maintain a 10:1:1 mole ratio of ammonia/epoxide/water, while ensuring a maximum 75% autoclave fill factor at room temperature.

Raney Nickel is not a particularly active amination catalyst; usually 6-10 wt% based on the amount of epoxide in the reactor is used. The solid catalyst should be well dispersed during production of the polyalkylenepolyamines giving good suspensions of the catalyst.

Example 1BPREPARATION OF C₁₄ POLYALKYLENEPOLYAMINE

-23-

1 The procedure of Example 1A was followed using 290.3 g of
2 a C₁₄ epoxide. The procedure yielded 314 g of a C₁₄
3 polyalkylenepolyamine as the product.

4

5 Example 1C

6 PREPARATION OF N-METHYLATED C₁₀ POLYALKYLENEPOLYAMINE

7

8 To 60 g of the C₁₀ polyalkylenepolyamine of Example 1A,
9 placed in a 1000 ml 3-necked round bottom flask sitting in
10 an ice bath, 189.6 g of 98% formic acid was slowly added
11 with constant stirring. The mixture was then removed from
12 the ice bath. To this mixture, 185.4 ml of 37%
13 formaldehyde solution was added. This new mixture was
14 then heated at reflux (100-110°C). After approximately 10
15 minutes, carbon dioxide began to form. Once the evolution
16 of carbon dioxide subsided, the reaction mixture was
17 heated continuously at 100°C for 16 hours.

18

19

Example 1D

20 FIRST PREPARATION OF N-METHYLATED C₁₄ POLYALKYLENEPOLYAMINE

21

22 A C₁₄ polyalkylenepolyamine was prepared as in Example 1B.
23 To 150 g of this C₁₄ polyalkylenepolyamine, in a 2000 ml 3-
24 necked round bottom flask sitting in an ice bath, 400 g of
25 98% formic acid was slowly added with constant stirring.
26 The mixture was then removed from the ice bath and 500 g
27 of 37% formaldehyde solution was added. This new mixture
28 was then heated at reflux (100-110°C). After
29 approximately 10 minutes, carbon dioxide began to form.
30 Once the evolution of carbon dioxide subsided, the
31 reaction mixture was heated continuously at 100°C for 16
32 hours. After cooling to room temperature, excess reagent
33 was removed under reduced pressure. The oily residue was
34 dissolved in conc. HCl and washed with toluene. The
35 aqueous layer was then basified with conc. NaOH and
36 extracted with toluene. The toluene was evaporated to

-24-

1 yield 158 g of a brown liquid product. The structure of
2 the product was confirmed by IR and NMR spectra.

3

4

Example 1E

5

SECOND PREPARATION OF N-METHYLATED

6

C₁₄ POLYALKYLENEPOLYAMINE

7

8 A C₁₄ polyalkylenepolyamine was prepared as in Example 1B.
9 A 50 g of this C₁₄ polyalkylenepolyamine (6.6% of N), and
10 19.55 g of 98% formic acid was mixed in 200 ml 3-neck
11 flask equipped with stirrer and condenser. The mixture
12 was heated to 100°C. To this mixture 12.33 g of solid
13 paraformaldehyde was added batchwise so that the
14 liberation of carbon dioxide was controlled at a
15 manageable rate. After carbon dioxide evolution subsided,
16 the reaction mixture was heated at 100-110°C for 8 hours.
17 The mixture was then cooled to room temperature and
18 diluted with 200 ml of toluene (or diethyl ether), and the
19 organic solution was washed with 100 ml of 5% aqueous
20 sodium hydroxide. The organic layer was dried (MgSO₄), and
21 solvent was removed in vacuo to give 70 g of an oily
22 product. The structure of product was confirmed by IR and
23 NMR spectra. The melting point, i.e., second DSC endpoint,
24 for this product is 123°F.

25

26

Example 1F

27

PREPARATION OF N-METHYLATED AND

28

C₁₆ POLYALKYLENEPOLYAMINES

29

30 A C₁₆ polyalkylenepolyamine was prepared from the C₁₆
31 epoxide in a manner similar to Example 1A. The produce
32 had a melting point (DSC endpoint of 194°F. This produce was
33 methylated as in Example 1E. The DSC endpoint of this
34 produce was 109°F. As this example shows, the methylated
35 produce had a substantially lower melting point than the
36 starting polyalkylenepolyamine.

37

-25-

1 Example 2A

2 PREPARATION OF C₁₀ POLYALKYLENEPOLYAMINE
3 REACTION PRODUCT WITH ALPHA-CHLOROMETHYL PHOSPHORIC ACID
4

5 A mixture of 20 g of the C₁₀ polyalkylenepolyamine of
6 Example 1A (9.17 wt% N, 0.131 eq.), and 18.8 g of alpha
7 chloromethyl phosphoric acid in 100 ml of methyl t-butyl
8 ether solvent was heated at reflux (80°C) for 30 hours
9 under nitrogen. On removal of solvent it gave 36.5 g of a
10 brown viscous oil, which soon became a glassy solid.
11 Total Amine Value (TAV) analysis was consistent with the
12 expected structure. The dispersibility and corrosion
13 inhibition properties demonstrated by this product are
14 outlined in Table 1, Run 20.

15

16 Example 2B

17 PREPARATION OF C₁₄ POLYALKYLENEPOLYAMINE
18 REACTION PRODUCT WITH ALPHA-CHLOROMETHYL PHOSPHORIC ACID
19

20 The procedure of Example 2A was followed using the
21 N-methylated C₁₄ polyalkylenepolyamine of Example 1D or 1E.
22 The structure was checked by NMR and TAV analysis. The
23 dispersibility and corrosion inhibition properties
24 demonstrated by this product are outlined in Table 1 Run
25 35.

26

27 Example 3

28 PREPARATION OF C₁₀ POLYALKYLENEPOLYAMINE
29 REACTION PRODUCT WITH PHOSPHOROUS ACID AND FORMALDEHYDE
30

31 To a mixture of 20 g of C₁₀ polyalkylenepolyamine (9.17 wt
32 % N, 0.131 eq.), 12.99 ml (21.45 g, 0.262 mole) of
33 phosphorous acid, and 21.23 ml of formaldehyde (37%, 0.262
34 mole) in a 3 neck round bottom flask, 52.32 ml of
35 concentrated HCl was added dropwise. The reaction was
36 slightly exothermic. After the addition of HCl, the
37 mixture was heated at 100°C for 5 hours. Aqueous work up

-26-

1 and evaporation gave a solid product of mp 75-88°C. The
2 structure was checked by NMR and TAV analysis. The
3 dispersibility and corrosion inhibition properties
4 demonstrated by this product are outlined in
5 Table 1, Run 21.

6

7

Comparative Example 4

8

PREPARATION OF C₁₀ POLYALKYLENEPOLYAMINE

9

REACTION PRODUCT WITH DIMETHYL CARBONATE

10

11 Twenty (20) ml of dimethyl carbonate was added to a
12 solution of 20 g of C₁₀ polyalkylenepolyamine (9.17% of N,
13 0.131 eq.), in 100 ml of anhydrous isopropyl alcohol. The
14 reaction mixture was heated at reflux under nitrogen
15 atmosphere for 48 hours. After removal of solvent in
16 vacuum, 34 g of yellow brownish solid was obtained. TAV
17 of product was 123.04 (TAV of starting amine was 367).
18 The dispersibility of this product was poor, see Table 1,
19 Run 22. This product is not a good water-dispersible
20 corrosion inhibitor.

21

22

Example 5A

23

PREPARATION OF C₁₂ POLYALKYLENEPOLYAMINE

24

REACTION PRODUCT WITH DIMETHYL SULFATE

25

26 A mixture of 20 g of a C₁₂ polyalkylenepolyamine (8.15%
27 of N) prepared in the manner of Example 1A, and 15.41 g
28 (0.1223 mole) of dimethyl sulfate was dissolved in 100 ml
29 of anhydrous isopropyl alcohol. The mixture was heated at
30 reflux under nitrogen gas for 5 hours. On removal of
31 solvent it yielded 29.4 g of amber glassy product.
32 Product was checked by NMR and TAV analysis. The
33 dispersibility and corrosion inhibition properties
34 demonstrated by this product are outlined in Table 1, Run
35 25.

-27-

Example 5B

PREPARATION OF C₁₄ POLYALKYLENEPOLYAMINE

REACTION PRODUCT WITH DIMETHYL SULFATE

5 The procedure of Example 5A was followed using the
6 N-methylated C₁₄ polyalkylenepolyamine of Example 1D or 1E
7 Product was checked by NMR and TAV analysis. The
8 dispersibility and corrosion inhibition properties
9 demonstrated by this product are outlined in Table 1, Run
10 35.

Example 6

PREPARATION OF C₁₄ POLYALKYLENEPOLYAMINE

REACTION PRODUCT WITH BENZYL CHLORIDE

15 A mixture of 20 g of C₁₄ polyalkylenepolyamine (6.99%
16 of N, 0.099 eq.), and 13.28 g of benzyl chloride (0.105
17 mole) in 100 ml of isopropyl alcohol was heated at reflux
18 for
19 15 hours. Reaction was monitored with reverse phase thin
20 layer chromatography (TLC). After completion of reaction,
21 solvent was removed under vacuum. It gave 30.48 g of a
22 viscous liquid. Structure was confirmed by IR, NMR, and
23 Total Amine Value analysis (=zero). The dispersibility
24 and corrosion inhibition properties demonstrated by this
25 product are outlined in Table 1, Run 26.

Example 7A

PREPARATION OF C₁₆ POLYALKYLENEDIPOLYAMINE

REACTION PRODUCT WITH METHYL CHLORIDE

31 A solution of 20 g of C₁₆ polyalkylenepolyamine (TAV=240),
32 in 80 ml of isopropyl alcohol was placed in an autoclave.
33 To this solution 9.68 g (100% excess) of methyl chloride
34 was charged. The mixture was heated at 100°C with 500 psi
35 of nitrogen pressure for 10 hours with vigorous stirring.
36 Reaction was monitored with reverse phase TLC. After
37 removal of solvent and excess methyl chloride, 23.35 g of

-28-

1 solid product was obtained, mp $>250^{\circ}\text{C}$. Product was
2 checked by NMR and TAV (= 6). The corrosion inhibition
3 properties demonstrated by this product are outlined in
4 Table 1, Run 29.

5

6

Example 7B

7

PREPARATION OF C_{14} POLYALKYLENEPOLYAMINE

8

REACTION PRODUCT WITH METHYL CHLORIDE

9

10 The procedure of Example 2A was followed using the N-
11 methylated C_{14} polyalkylenepolyamine of Example 1C or 1D.
12 Results Table 1 Run 35.

13

14

Comparative Example 8

15

PREPARATION OF C_{20-24} POLYALKYLENEPOLYAMINE

16

REACTION PRODUCT WITH CHLOROACETAMIDE

17

18 A mixture of 20 g of C_{20-24} polyalkylenepolyamine (4.8%
19 N, 0.0685 eq.), and 6.55 g (0.07 mole) of chloroacetamide
20 in 100 ml of toluene was heated at reflux under nitrogen
21 for
22 52 hours. After cooling to room temperature, the solid
23 precipitates were filtered and dried in a vacuum oven
24 (50°C). It yielded 16.5 g of product, mp $75-120^{\circ}\text{C}$; TAV =
25 16.9, with 7.32% nitrogen. The dispersibility of this
26 product is poor, see Table 1, Run 32. This product was
27 not a good water dispersible corrosion inhibitor.

28

29

Example 9A

30

PREPARATION OF C_{10} POLYALKYLENEPOLYAMINE

31

REACTION PRODUCT WITH ETHYLENE OXIDE

32

33 A mixture of 25 g of C_{10} polyalkylenepolyamine (10% of
34 nitrogen, 0.178 eq.), 7.86 g of anhydrous ethylene oxide
35 (0.178 eq.), 40 ml of acetonitrile, and 40 ml of t-butyl
36 methyl ether was charged into a 100 ml autoclave cooled by
37 dry ice and acetone bath. The mixture was heated to 86°C

-29-

1 and vigorously stirred for 4 hours. The autoclave was
2 cooled to room temperature and vented. The mixture was
3 placed on the rotatory evaporator to remove solvents. It
4 yielded 30 g of brown oil as product (TAV=174, 6.82% of
5 N). The product was tested as a corrosion inhibitor
6 without further purification. The dispersibility and
7 corrosion inhibition properties demonstrated by this
8 product are outlined in Table 1, Run 23.

9

10

Example 9B

11

PREPARATION OF C₁₀ POLYALKYLENEPOLYAMINE

12

REACTION PRODUCT WITH 10 ETHYLENE OXIDE EQUIVALENTS

13

14 A mixture of 25 g of C₁₀ polyalkylenepolyamine, (10% of
15 nitrogen, 0.178 eq.), prepared in the manner as described
16 in Example 1A, 78.6 g of anhydrous ethylene oxide (1.78
17 eq.), 1 ml of trifluoroacetic acid, 200 ml of acetonitrile,
18 and 100 ml of t-butyl methyl ether is charged into a 500
19 ml autoclave cooled by a dry ice/acetone bath. The
20 mixture is heated to 86°C and vigorously stirred for 4
21 hours. The autoclave is cooled to room temperature and
22 vented. The liquid is then placed on a rotatory
23 evaporator and yields a brown oily product. This product
24 is an effective corrosion inhibitor.

25

26

Example 10A

27

PREPARATION OF C₁₀ N-METHYLATED POLYALKYLENEPOLYAMINE

28

REACTION PRODUCT WITH BENZYL CHLORIDE

29

30 A mixture of 20 g of C₁₀ N-methylated polyalkylenepolyamine
31 (9.61% of N, 0.137 eq.) prepared in Example 1B, and 18.24
32 g of benzyl chloride (0.144 mole) in 100 ml of isopropyl
33 alcohol was heated at reflux for 15 hours. Reaction was
34 monitored with reverse phase TLC. After completion of
35 reaction, solvent was removed under vacuum. It gave 34.4
36 g of a brownish, oily, liquid product. Structure was
37 confirmed by IR, NMR, and TAV analysis (=zero). The

-30-

1 dispersibility and corrosion inhibition properties
2 demonstrated by this product are outlined in Table 1, Run
3 24.

4

5

Example 10B

6 FIRST PREPARATION OF C₁₄ N-METHYLATED POLYALKYLENEPOLYAMINE
7 REACTION PRODUCT WITH BENZYL CHLORIDE

8

9 A mixture of 15 g of C₁₄ N-methylated polyalkylenepolyamine
10 (7.14% of N, 0.0765 eq.) prepared in Example 1C, and 9.68
11 g of benzyl chloride (0.0765 eq.) in a solution of 80 ml
12 t-butyl methyl ether and 20 ml of acetonitrile was heated
13 at reflux for 15 hours. Reaction was monitored with
14 reverse phase TLC. After completion of reaction, solvent
15 was removed under vacuum. It gave 20 g of a brownish,
16 oily, viscous product. Structure was confirmed by IR,
17 NMR, and TAV analysis (which was zero). Product was
18 checked by NMR and TAV analysis. The dispersibility and
19 corrosion inhibition properties demonstrated by this
20 product are outlined in Table 1, Run 34.

21

22

Example 10C

23

24

SECOND PREPARATION OF C₁₄ N-METHYLATED
POLYALKYLENEPOLYAMINE REACTION PRODUCT
WITH BENZYL CHLORIDE

25

26

27 A mixture of 25 g of C₁₄ N-methylated polyalkylenepolyamine
28 (5.49% of N, 0.098 eq.) preparation in Example 1E, and
29 11.17 g of benzyl chloride (0.088 eq.) in a solution of 50
30 ml of isopropyl alcohol was heated at reflux for 15 hours.
31 Reaction was monitored with reverse phase TLC. After
32 completion of reaction, solvent was removed under reduced
33 pressure. It gave 36 g of viscous oil as product.
34 Structure was confirmed by IR, NMR, and TAV analysis
35 (which was zero).

36

-31-

1 After cooling to room temperature, excess reagent was
2 removed under reduced pressure. The oily residue was
3 dissolved in conc. HCl and washed with toluene. The
4 aqueous layer was then basified with conc. NaOH and
5 extracted with toluene. The toluene was evaporated to
6 yield 64.5 g of a brown oily product. The structure of
7 the product was confirmed by IR and NMR spectra. Product
8 was checked by NMR and TAV analysis. The dispersibility
9 and corrosion inhibition properties demonstrated by this
10 product are outlined in Table 2, Run 34.

11

12 Example 11

13 BENZYL CHLORIDE QUATS OF METHYLATED AMINES

14

15 Additional benzyl chloride quats were prepared from a
16 methylated C₁₆ polyalkylenepolyamine (to give a quat having
17 14 carbon atoms in the alkyl group side chain) and from a
18 methylated C₂₀₋₂₄ polyalkylenepolyamine (to give a quat
19 having 18 to 22 carbon atoms in the alkyl group side
20 chain).

21

22 TABLE 2

23

24 PERCENT CORROSION PROTECTION AT 50 PPM

25

No. of Carbons in Alkyl Group	Methylated Amine	Benzyl. Chloride Quat
8	96.8	96.1
12	90.4*	95.8
14	79.2*	97.2
18-22	-	95.0

32

33 * Run at 1000 PPM conc. instead of 50 PPM (as 50
34 PPM was too low a level to observe corrosion
35 protection for these amines).

36

37

38 Table 2 above summarizes the results for the continuous
39 wheel test using polyalkylenepolyamines having a variety

-32-

1 of carbon atoms in the alkyl group. (Note: a C_{14}
2 polyalkylenepolyamine produces a quat with 12 carbon atoms
3 in the alkyl group). As can be seen, the benzyl chloride
4 quats of these methylated amines are excellent corrosion
5 inhibitors at very low concentrations (50 ppm).

6

7

Example 12

8

WATER DISPERSIBILITY TEST USING NACE BRINE

9

10 The water dispersibility test evaluates the dispersibility
11 of corrosion inhibitor formulations used in water-based
12 environments. Each formulation's dispersibility behavior
13 was monitored for 24 hours in standard NACE Brine at a
14 90:10 ratio of brine to corrosion inhibitor formulation.
15 The observations were tabulated so that the quality of the
16 dispersions could be rated and compared on a numeric
17 scale. The lower the rating, the more dispersible the
18 formulation in aqueous environments.

19

20 In running this test, 45 ml of NACE Brine (which consists
21 of 365.6 g of NaCl, 15.4 g of $CaCl_2$ and 7 g of $MgCl_2$ per
22 liter of water) was added to a 50 ml closed-top graduated
23 cylinder.

24

25 Five ml of formulation consisting of 10% corrosion
26 inhibitor in isopropyl alcohol was then added to the NACE
27 Brine. If the formulation dispersed immediately, it was
28 given a rating of zero.

29

30 If the formulation did not immediately disperse, the
31 mixture was inverted once. It was noted whether the
32 formulation dispersed in the NACE Brine at this point. If
33 it failed to do so, the cylinder was inverted an
34 additional 30 times and observed for any signs of
35 dispersibility.

-33-

1 Each sample which had to be inverted was monitored after
2 both 10 minutes and 24 hours to check for phase
3 separations. Specifically, it was ascertained whether any
4 cream layers, oil layers, or flocculation formulations
5 were present. If so, the level of each layer (in ml) was
6 measured. A cream layer is a milky or opaque combination
7 of the oil and brine phases and could be twice the volume
8 of the originally added formulation. An oil layer
9 appeared as a clearly defined oil phase separated out on
10 top of the brine or cream layer. Flocculation was
11 observed as a separation of solid material and could be
12 present in either a cream layer or oil layer.

13

14 The numeric ratings used to evaluate the formulation's
15 dispersibility were based upon each sample's behavior at
16 three time categories during the test.

17

18 A) Phase Behavior Upon Immediate Dissolution.

19 B) Phase Behavior After 10 Minutes.

20 C) Phase Behavior After 24 Hours.

21

22 At each stage, the solutions could exhibit the following
23 four types of properties: 1) good dispersions (i.e., one
24 phase either clear or opaque); 2) cream layer formation;
25 3) oil layer formation; or 4) flocculation formation. The
26 overall rating scale combines the individual
27 dispersibility results obtained at each of the three
28 stages. It is rated heavily against flocculation and oil
29 layer formation, the most telling signs of a lack of
30 dispersibility.

31

32 A) Immediate Dissolution Calculation

33	<u>Rating Units</u>	<u>Comments</u>
34		
35	0	Self-disperses
36		
37	2	One turn dispersion,
38		one phase after 24 hours
39		

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1	4	One turn dispersion,
2		separation in 24 hours
3		
4	6	One turn dispersion,
5		separation in 10 minutes
6		
7	8	30 turn dispersion,
8		separation in 24 hours
9		
10	10	30 turn dispersion,
11		separation in 10 minutes
12		
13	12	30 turns, no dispersion
14		
15		

16 Note: There are a maximum of 12 Rating Units at this
17 stage.

18

19 B) 10-Minute Calculation

20

21 Cream Formation: 2 Rating Units for each ml of cream
22 measured, up to a maximum of 10
23 Rating Units.

24

25 Cream & Oil Formation: The maximum number of Rating Units
26 for cream formation (10 Rating
27 Units) added to 4 Rating Units for
28 each ml of oil measured. If any
29 oil is detected, even if it does
30 not amount to 1 ml, 1 Rating Unit
31 is added.

32

33 Flocculation: Any flocculation results in 50
34 Rating Units.

35

36 C) 24-Hour Calculation

37

38 While it is important for a formulation to stay
39 dispersed indefinitely, its behavior after 10
40 minutes is more important. The 24-hour
41 calculation is weighted to reflect this fact.

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1 The 24-hour evaluation was done the same way as
2 the 10-minute evaluation -- except that the
3 resulting number was then weighted by
4 subtracting the 10-minute number from it and
5 dividing by 2; that is, (24 Hr-10 Min.)/2.

6

7 Total Dispersion Calculation

8

9 The total number of Rating Units for a given
10 formulation are obtained by combining the individual
11 numbers calculated individually for A, B, and C as
12 detailed above. The lower the number, the better
13 the dispersibility of the formulation in aqueous
14 media.

15

16

Example 13

17

 SAMPLE WATER DISPERSIBILITY TEST CALCULATION

18

19 A sample formulation was tested which showed the following
20 dispersion characteristics: 1) It did not disperse
21 immediately and only went into solution after 30
22 inversions; 2) It separated out after 10 minutes,
23 revealing 3 ml of cream and 2 ml of oil; and 3) After 24
24 hours it had 1 ml of cream and 3 ml of oil.

25

26 Total Dispersion Calculation

27

28 A) Immediate Dissolution Calculation: 30 turn
29 dispersion with separation in 10 minutes yields
30 10 Rating Units

31

32 B) 10-Minute Calculation

33

34 Since cream and oil are both present after 10
35 minutes we start with the base level of 10
36 Rating Units. To this we add 4 Rating Units
37 for each ml of oil present.

-36-

1 Therefore,
2 10-Minute Scale = $(2 \times 4) + 10 = \underline{18 \text{ Rating}}$
3 Units

4
5 C) 24-hour Calculation

6
7 We initially calculate the 24-hour number in
8 the same manner as the 10-minute number. Since
9 cream and oil are both present after 24-hours,
10 we start with the base level of 10 Rating
11 Units. To this we add 4 Rating Units for each
12 ml of oil present.

13
14 Therefore, since 3 ml of oil are present:
15 24-hour Scale = $(3 \times 4) + 10 = 22 \text{ Rating Units}$

16
17 We then need to calculate the 24-hour weighted
18 number by subtracting the 10-minute calculation
19 and dividing by two.

20
21 24-hour weighted Number Scale:
22 $(22-10)/2 = \underline{2 \text{ Rating Units}}$

23
24 Total Dispersibility Rating

25
26 Total Dispersibility = $A+B+C = 10+18+2 = \underline{30}$
27 Rating Units

28
29 Table 1 below summarizes the Water Dispersibility Test
30 results for the derivatized polyalkylenepolyamines which
31 are the subject of this invention.

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Example 14WHEEL TEST EVALUATION OF DERIVATIZED
POLYALKYLENEPOLYAMINES AS CORROSION
INHIBITORS FOR CO₂ CORROSION

The Wheel Test is an industry standard test procedure used to evaluate corrosion inhibitors. The test is described in the National Association of Corrosion Engineers (NACE) publication ID182. The procedures followed in this example are essentially the same as those described in the NACE publication and are discussed below.

The test fluid consisted of 98% synthetic brine as described in NACE publication ID182 and 2% deodorized kerosene. The brine was flushed with nitrogen, then saturated with CO₂ gas at room temperature.

Test coupons were 5 ml thick mild steel shimstock and were sandblasted in a ball mill and tared prior to use. The test coupon, test fluid, and inhibitor were placed in a 7-oz. juice bottle taking care to avoid oxygen contamination. The inhibitor was added at a level of 125 ppm. The bottles were capped and placed on a rotating wheel mounted in a 90°C oven for 24 hours.

Following the test, the coupons were removed from the bottles, rinsed with soap and water, dipped in 10% hydrochloric acid, and rinsed with water. A plastic wool pad was used to scrub any remaining corrosion products from the coupon, after which the coupon was rinsed, dried, and weighed to determine the weight loss. The percent corrosion inhibition provided by the inhibitor was calculated with reference to the weight loss of an uninhibited coupon, according to the following formula:

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$$\% \text{ Inhibition} = \frac{(\text{Uninhibited weight loss} - \text{Inhibited weight loss})}{\text{Uninhibited weight loss}}$$

Table 1 below summarizes the corrosion inhibition test results for the derivatized polyalkylenepolyamines which are the subject of this invention.

As can be seen by these results, the derivatized polyalkylenepolyamine compositions which were found to be most water soluble proved to be excellent corrosion inhibitors.

TABLE 1 -- Results at 125 ppm

RUN NO.	REACTANTS	DISPERSIBILITY RATING	CORROSION
<u>INHIBITION^{2,3}</u>			
C₁₀ POLYALKYLENEPOLYAMINE			
20	- ALPHA-CHLOROMETHYL PHOSPHORIC ACID	5	95
21	- PHOSPHOROUS ACID AND FORMALDEHYDE	5	96
22*	- DIMETHYL CARBONATE	NOT DISPERSIBLE	--
23	- ETHYLENE OXIDE	SLIGHTLY DISPERSIBLE	87
C₁₀ N-METHYLATED POLYALKYLENEPOLYAMINE			
24	- BENZYL CHLORIDE	2	98
C₁₂ POLYALKYLENEPOLYAMINE			
25	- DIMETHYL SULFATE	4	94
C₁₄ POLYALKYLENEPOLYAMINE			
26	- BENZYL CHLORIDE	5	93
27	- DIMETHYL SULFATE	4	94
28	- ETHYLENE OXIDE	21	--
C₁₆ POLYALKYLENEPOLYAMINE			
29	- METHYL CHLORIDE	NOT MEASURED	96

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1 C₂₀₋₂₄ POLYALKYLENEPOLYAMINE

2

3	30	- ETHYLENE OXIDE	20	--
4	31	- BENZYL CHLORIDE	6	97
5	32*	- CHLOROACETAMIDE	NOT	--
6			DISPERSIBLE	

7 -----

8 * COMPARATIVE EXAMPLES

- 9
- 10 1. At 1% for 24 hours per Examples 12 and 13.
- 11 2. Per Example 14 at 125 PPM.
- 12 3. If dispersibility was poor, meaningful corrosion inhibition data
- 13 could not be obtained.
- 14
- 15

16 TABLE 1A -- Results at 50 ppm

17

18 RUN			DISPERSIBILITY	CORROSION
19 NO.	REACTANTS		RATING	
20	INHIBITION ^{2,3}			
21				
22	C ₁₄ N-METHYLATED			
23	POLYALKYLENEPOLYAMINE			
24				
25	34 - BENZYL CHLORIDE		<4	95
26	35 - ALPHA-CHLOROMETHYL			
27	PHOSPHORIC ACID		<4	93
28	36 - METHYL CHLORIDE		<4	95
29	37 - DIMETHYL SULFATE		<4	94
30				
31				
32				

33 * COMPARATIVE EXAMPLES

- 34
- 35 1. At 1% for 24 hours per Examples 12 and 13.
- 36 2. Per Example 14 at 50 PPM.
- 37 3. If dispersibility was poor, meaningful corrosion inhibition data
- 38 could not be obtained.
- 39

1 WHAT IS CLAIMED IS:

2

3 1. Derivatives of polyalkylenepolyamines useful as
4 corrosion inhibitors in aqueous media, comprising:

5

6 a composition produced by reacting

7

8 a) a derivatizing agent, which is either an
9 alkylating agent or an alkylene oxide; with

10

11 b) a starting polyalkylenepolyamine comprising a
12 mixture of:

13

14 (i) at least one C-alkyl-ethylene diamine; and

15 (ii) at least one di-(C-alkyl)-

16 diethylenetriamine;

17

18 wherein each C-alkyl group on the ethylene diamine

19 and the diethylenetriamine independently contain

20 between 8-26 carbon atoms;

21

22 thereby producing derivatized polyalkylenepolyamines.

23

24 2. The composition according to Claim 1 wherein said
25 polyalkylenepolyamine derivatives are either water
26 soluble or have a water dispersibility rating under
27 10.

28

29 3. The composition according to Claim 1 wherein said
30 polyalkylenepolyamine derivatives are amine salts.

31

32 4. The composition according to Claim 1 wherein said
33 polyalkylenepolyamine derivatives are quaternary
34 amine salts.

35

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- 1 5. The composition according to Claim 1 wherein said
2 starting polyalkylenepolyamines are N-methylated
3 polyalkylenepolyamines.
4
- 5 6. The composition according to Claim 1 wherein said
6 polyalkylenepolyamine derivatives have a corrosion
7 inhibition rating in aqueous media above 90%.
8
- 9 7. The composition according to Claim 1 wherein the
10 alkylating agent, BX, has B selected from the group
11 consisting of hydrogen, an alkyl or aryl group,
12 benzyl, or alkylcarboxylate and X selected from the
13 group consisting of a halogen, sulfonate, carbonate,
14 phosphonate or other correspondingly good anion.
15
- 16 8. The composition described in Claim 7 where the
17 alkylating agent is an alkyl halide.
18
- 19 9. The composition described in Claim 8 where the
20 alkylating agent is methyl chloride.
21
- 22 10. The composition described in Claim 8 where the
23 alkylating agent is benzyl chloride.
24
- 25 11. The composition described in Claim 8 where the
26 alkylating agent is alpha-chloroacetic acid.
27
- 28 12. The composition described in Claim 8 where the
29 alkylating agent is alpha-chloromethyl phosphoric
30 acid.
31
- 32 13. The composition described in Claim 7 where the
33 alkylating agent is dimethyl sulfate.
34
- 35 14. The composition described in Claim 7 where the
36 alkylating agent is a mixture of phosphorous acid and
37 formaldehyde.

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- 1 15. The composition of derivatized polyalkylenepolyamines
2 according to Claim 1 or 4 wherein each C-alkyl group
3 contains between 8 to 16 carbon atoms.
4
- 5 16. The composition of derivatized polyalkylenepolyamines
6 according to Claim 15 wherein said C-alkyl group
7 contains 12 or 14 carbon atoms.
8
- 9 17. The composition according to Claim 1 wherein said
10 polyalkylenepolyamine derivatives are obtained by
11 reacting the starting polyalkylenepolyamine mixture
12 with an alkylene oxide.
13
- 14 18. The composition described in Claim 17 where the
15 reactant is ethylene oxide.
16
- 17 19. A composition comprising a polyderivatized mixture
18 of:
19
- 20 (i) at least one C-alkyl-ethylene diamine; and
21
- 22 (ii) at least one di-(C-alkyl)-diethylenetriamine;
23
- 24 wherein each C-alkyl group on the ethylene
25 diamine and the diethylenetriamine
26 independently contain between 8-26 carbon
27 atoms.
28
- 29 20. The composition of Claim 19 wherein substantially all
30 the nitrogen atoms of said components (i) and (ii)
31 are positively charged.
32
33

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1 21. A composition containing derivatives of
2 polyalkylenepolyamines useful as corrosion inhibitors
3 in aqueous media, comprising:

4
5 a mixture of:

- 6
7 (i) at least one C-alkyl-ethylene diamine
8 polyammonium salt; and
9
10 (ii) at least one di(C-alkyl)-diethylenetriamine
11 polyammonium salt;

12
13 wherein each C-alkyl group on the ethylene
14 diamine and the diethylenetriamine
15 independently contain between 8-26 carbon
16 atoms.

17
18 22. The composition of Claim 21 wherein substantially all
19 the nitrogen atoms of said components (i) and (ii)
20 are positively charged.

21
22 23. A composition containing derivatives of
23 polyalkylenepolyamines useful as corrosion inhibitors
24 in aqueous media, comprising:

25
26 a mixture of:

- 27
28 (i) at least one C-alkyl-ethylene diamine poly-N-
29 ethoxylate; and
30 (ii) at least one di-(C-alkyl)-diethylenetriamine
31 poly-N-ethoxylate;

32
33 wherein each C-alkyl group on the ethylene
34 diamine and the diethylenetriamine
35 independently contain between 8-26 carbon
36 atoms.

37

- 1 24. The composition of Claim 23 wherein substantially all
2 the nitrogen atoms of said components (i) and (ii)
3 are ethoxylated.
4
- 5 25. A method of inhibiting corrosion of a corrodible
6 metal wherein a corrosion inhibiting effective amount
7 of the composition of polyalkylenepolyamine
8 derivatives described in one of Claims 1, 19, 21 or
9 23 is contacted directly with the potentially
10 affected metal part.
11
- 12 26. A method of inhibiting corrosion of corrodible metal
13 material used in oil field operations wherein a
14 corrosion inhibiting effective amount of the
15 composition of polyalkylenepolyamine derivatives
16 described in one of Claims 1, 19, 21 or 23 is
17 injected directly into the well being drilled.
18
- 19 27. A composition according to Claim 7 wherein the C-
20 alkyl group contains 12 or 14 carbon atoms and the
21 alkylating agent, BX, has B selected from the group
22 consisting of lower alkyl or benzyl and X selected
23 from the group consisting of chloride, bromide or
24 methyl sulfonate.
25
- 26 28. A composition comprising N-methylated
27 polyalkylenepolyamines which are useful for preparing
28 compositions as described in Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US92/08036**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :C23F 11/14

US CL :252/8.555, 8.554, 390,392; 422/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/8.555, 8.554, 390,392; 422/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,900,458 (SCHROEDER ET AL.), 13 FEBRUARY 190, entire document.	1-22,25-28
Y	US,A, 3,349,032 (KRIEG), 24 OCTOBER 1967, see col. 2 lines 60-71, col. 3 lines 23-51.	1-22,25-28
Y	US,A, 3,200,106 (DICKSON, ET AL), 10 AUGUST 1965, See col. 3 lines 1-23	23-25
Y	US,A, 2,761,843 (BROWN), 04 SEPTEMBER 1956. See col. 3 lines 55-74.	1-22,25-28

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

01 DECEMBER 1992

Date of mailing of the international search report

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